Copper(II) Nitrate-(±)-1-Phenylethylamine

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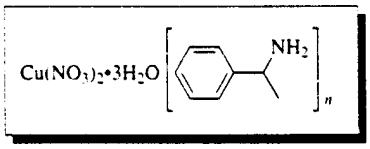
Copper(II) Nitrate-(±)-1-Phenylethylamine[1]



$(Cu(NO_3)_2 \cdot 3H_2O)$
[10031-43-3] $H_6CuN_2O_9$ (MW 241.60)
$((\pm)\text{-PhCH(Me)NH}_2)$
[618-36-0] $C_8H_{11}N$ (MW 121.18)

(reagent for the oxidative coupling of phenols[2])

Physical Data: $Cu(NO_3)_2 \cdot 3H_2O$: mp 114 °C. (±)-1-Phenylethylamine: bp 185 °C/756 mmHg; *d* 0.95 g cm^{-3}. The exact structure of the copper(II) complex is unknown; the number of phenylethylamine ligands is preferentially 4 (*n* = 4).

Form Supplied in: the reagent is prepared in situ; both compounds are commercially available. (±)-1-Phenylethylamine is a colorless oil; copper(II) nitrate trihydrate is a blue crystalline deliquescent material.

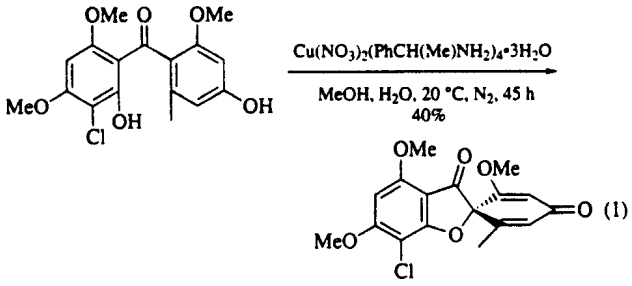
Analysis of Reagent Purity: $Cu(NO_3)_2 \cdot 3H_2O$: > 99%. (±)-1-Phenylethylamine: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.37 (d, *J* = 6.4 Hz, 3H), 4.07 (q, *J* = 6.7 Hz, 1H), 7.19-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ 25.2 (q), 50.8 (d), 125.2 (d), 126.3 (d), 127.9 (d), 147.3 (s).

Preparative Methods: prepared in situ by complexation of copper(II) nitrate with 4 equiv of (±)-1-phenylethylamine in methanol under inert atmosphere.[1,2]

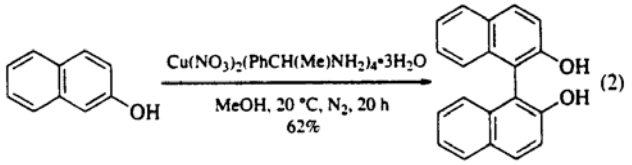
Handling, Storage, and Precautions: (±)-1-phenylethylamine is stable when stored in a sealed container under nitrogen.

General Considerations. The copper(II) nitrate-(±)-1-phenylethylamine reagent (**1**) is a typical example of a number of copper(II) amine oxidizing agents.[1-3] Reagent (**1**) can effect the oxidative coupling of phenols under anaerobic conditions. Both C-C and C-O coupled products can be obtained. Characteristic examples are given.

Synthesis of Dehydrogriseofulvin. Reaction of (**1**) with bisphenols leads to intramolecular C-O coupled products (eq 1).[1]



Synthesis of 1,1′-binaphthalene-2,2′-diols. The oxidative dimerization of 2-naphthols with (**1**) provides 1,1′-binaphthols (eq 2).[2]



Unsymmetrical 1,1′-binaphthalene-2,2′-diols are formed in 80-97% yield by oxidative cross-coupling of differently substituted 2-naphthols mediated by related Cu^{II}-primary amine complexes.[3b] (*S*)-(-)-1,1′-Binaphthalene-2,2′-diol and (*S*)-(-)-10,10′-dihydroxy-9,9′-biphenanthryl have been prepared with optical purities up to 98% by a similar oxidative coupling using chiral nonracemic primary amines.[1,3a,3d]

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